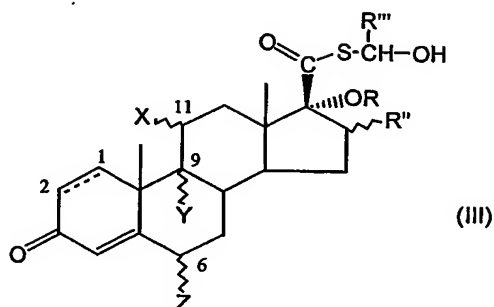


## CLAIMS

1. Compounds of general formula (III):



wherein

R is H or COR' and R' is selected from the group consisting of an alkyl group, linear or branched, having from 1 to 6 carbon atoms;

R'', in alpha or beta position with respect to the plane of the steroid reticule, is selected from the group consisting of H, an alkyl group, linear or branched, having from 1 to 5 carbon atoms; or

OR and R'', taken together, form a 16 $\alpha$ ,17 $\alpha$ -isopropylidendioxy group or higher 16 $\alpha$ ,17 $\alpha$ -alkylidendioxy groups, preferably having from 4 to 6 carbon atoms;

R''' is selected from the group consisting of H, an alkyl group having from 1 to 6 carbon atoms, a phenyl or substituted phenyl group, an aralkyl or substituted aralkyl group;

X, Y and Z, in alpha or beta position with respect to the plane of the steroid reticule, equal or different from each other, are selected from the group consisting of H, OH, Cl, F, and a carbonyl group, or

X and Y, taken together, are an epoxide group or form a double bond between the positions 9 and 11;

and wherein between the positions 1 and 2 a double bond may be present.

2. Compounds according to claim 1, selected from the group consisting of:

S-hydroxymethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (5);

S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (11);

S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (17);

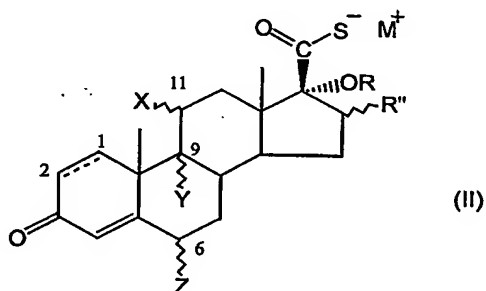
S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene-17 $\beta$ -carbothioate (21);

- 5 S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (27); and

S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (33).

3. Process for the preparation of compounds of general formula (III) comprising the following steps:

d) reaction of aldehydes of formula R'''CHO, wherein R''' is defined as above for the compound of formula (III), said aldehydes being possibly in the form of acetal, with a compound of general formula (II)



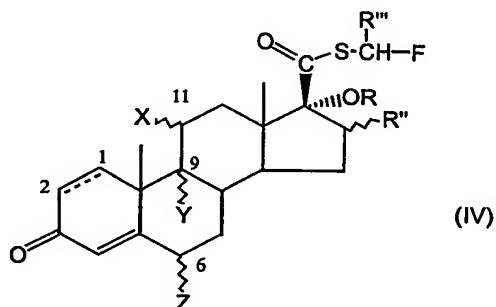
in which M<sup>+</sup> is an ammonium or aminic ion, or M is H or an alkaline metal, to give a compound of general formula (III), said reaction being possibly carried out in the presence of strong mineral acids, when M is an alkaline metal or M<sup>+</sup> is an ammonium or aminic ion.

4. Process according to claim 3, wherein in the reaction of step d) the strong mineral acid, when present, is hydrochloric acid.

5. Process according to claim 3, wherein the said aldehyde in the reaction of step d) is formaldehyde.

6. Process according to claim 3, further comprising a reaction of selective fluorination of the hydroxylic group in alpha position with respect to the sulphur

atom in compounds of general formula (III), reaction in step e) after step d), to give compounds of general formula (IV):



where R, R'', R''', X, Y and Z have the same meaning as above, wherein the said  
 5 reaction of selective fluorination is carried out with nucleophilic fluorination reagents.

7. Process according to claim 6, wherein the nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.

10 8. Process for the preparation of S-hydroxymethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (5) according to claim 3, wherein the compound of general formula (II) is 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (4) which is made to react in step d) with formaldehyde to  
 15 give S-hydroxymethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (5).

9. Process according to claim 8, wherein the starting reagent, 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (4) is obtained by means of a process comprising the  
 20 following steps:

a) reaction of 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -hydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (1) with propionyl chloride in the presence of triethylamine to give 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (2);

- b) reaction of 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (2) coming from step a) with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoiloxycarbonyl-6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene (3);
- 5 c) reaction of 17 $\beta$ -N,N-dimethylthiocarbamoiloxycarbonyl-6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene (3) coming from step b) with diethylamine to give 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (4).
- 10 10. Process according to claim 8, further comprising a reaction of selective fluorination of the hydroxylic group in alpha position with respect to the sulphur atom of S-hydroxymethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (5), reaction in step e) after step d), to give S-fluoromethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (6), wherein the reaction of
- 15 selective fluorination is carried out with nucleophilic fluorination reagents.
11. Process according to claim 10, wherein the nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.
- 20 12. Process for the preparation of S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (11) according to claim 3, wherein the compound of general formula (II) is 9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (10) which is made to react in step d) with formaldehyde to give S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-
- 25 3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (11).
13. Process according to claim 12, wherein the starting reagent, 9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (10) is obtained by means of a process comprising the following steps:

a) reaction of 9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -hydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (7) with propionyl chloride in the presence of triethylamine to give 9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (8);

5 b) reaction of 9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (8) coming from step a) with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene (9);

10 c) reaction of 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene (9) coming from step b) with diethylamine to give 9 $\beta$ ,11 $\beta$ -epoxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (10).

14. Process according to claim 12, further comprising a reaction of selective fluorination of the hydroxylic group in position alpha with respect to the sulphur atom of S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (11), reaction in step e) after step d), to give S-fluoromethyl 9 $\beta$ ,11 $\beta$ -epoxy-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (12), wherein the reaction of selective fluorination is carried out with nucleophilic fluorination reagents.

20 15. Process according to claim 14, wherein the nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.

16. Process for the preparation of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (17)

25 according to claim 3, wherein the compound of general formula (II) is 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (16) which is made to react in step d) with formaldehyde to give S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (17).

30 17. Process according to claim 16, wherein the starting reagent, 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -

thiocarboxylate of diethylammonium (16) is obtained by means of a process comprising the following steps:

a) reaction of 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (13) with propionyl chloride in the presence of triethylamine to give 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (14);

b) reaction of 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (14) coming from step a) with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene (15);

c) reaction of 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene (15) coming from step b) with diethylamine to give 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -thiocarboxylate of diethylammonium (16).

18. Process for the preparation of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (17) according to claim 3, wherein the compound of general formula (II) is 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene acid (16a) which is made to react in step d) with formaldehyde to give S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (17).

19. Process according to claim 18, wherein the starting reagent, 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene (16a) is obtained by means of a process comprising the following steps:

a) reaction of 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (13) with propionyl chloride in the presence of triethylamine to give 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (14);

b) reaction of 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (14) coming from step a) with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene (15);

c') reaction of 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene (15) coming from step b) with sodium hydrogen sulphide followed by treatment with phosphoric acid to give 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene acid (16a).

20. Process according to claims 16 and 18, further comprising after step d) a step e) of reaction of selective fluorination of the hydroxylic group in position alpha with respect to the sulphur atom of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxy- androsta-1,4-diene-17 $\beta$ -carbothioate (17), to give S-fluoromethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (18), wherein the reaction of selective fluorination is carried out with nucleophilic fluorination reagents.

21. Process according to claim 20, wherein the nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.

22. Process for the preparation of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene-17 $\beta$ -carbothioate (21) according to claim 3, wherein the compound of general formula (II) is 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene acid (20) which is made to react in step d) with formaldehyde to give S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene-17 $\beta$ -carbothioate (21).

23. Process according to claim 22, wherein the starting reagent, 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene acid (20) is obtained by means of a process comprising the following steps:

b) reaction of 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid (13) with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene (19);

c') reaction of 17 $\beta$ -N,N-dimethylthiocarbamoiloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene (19) coming from step b) with sodium hydrogen sulphide followed by treatment with phosphoric acid to give 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxoandrosta-1,4-diene acid (20).

24. Process according to claim 22, further comprising after step d) a step e) of selective fluorination of the hydroxylic group in alpha position with respect to the sulphur atom of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene-17 $\beta$ -carbothioate (21), to give S-fluoromethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,17 $\alpha$ -dihydroxy-16 $\alpha$ -methyl-3-oxo-androsta-1,4-diene-17 $\beta$ -carbothioate (22), wherein the reaction of selective fluorination is carried out with nucleophilic fluorination reagents.

25. Process according to claim 24, wherein the said nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.

26. Process for the preparation of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (27) according to claim 3, wherein the compound of general formula (II) is 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide acid (26) which is made to react in step d) with formaldehyde to give S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate16,17-acetonide (27).

27. Process according to claim 26, wherein the starting reagent, 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide acid (26) is obtained by means of a process comprising the following steps:

- a') alkaline hydrolysis in the presence of air of 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ ,21-tetrahydroxy-1,4-pregnadiene-3,20-dione-16,17-acetonide-21acetate (23) to give 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic 16,17-acetonide acid (24);
- 5 b) reaction of 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic 16,17-acetonide acid (24) coming from step a') with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide (25);
- 10 c') reaction of 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide (25) coming from step b) with sodium hydrogen sulphide followed by treatment with phosphoric acid to give 17 $\beta$  carbothioic 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide acid (26).
- 15 28. Process according to claim 26, further comprising after step d) a step e) of selective fluorination of the hydroxylic group in position alpha with respect to the sulphur atom of S-hydroxymethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (27), to give S-fluoromethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-11 $\beta$ ,16 $\alpha$ ,17 $\alpha$ -trihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -
- 20 carbothioate 16,17-acetonide (28), wherein the reaction of selective fluorination is carried out with nucleophilic fluorination reagents.
29. Process according to claim 28, wherein the nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.
- 25 30. Process for the preparation of S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (33) according to claim 3, wherein the compound of general formula (II) is 17 $\beta$  carbothioic 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide acid (32) which is made to react in step d) with formaldehyde to give S-
- 30 hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (33).

31. Process according to claim 30, wherein the starting reagent, 17 $\beta$  carbothioic 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide acid (32) is obtained by means of a process comprising the following steps:

a') alkaline hydrolysis in the presence of air of 6 $\alpha$ ,9 $\alpha$ -difluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ ,21-trihydroxy-1,4-pregnadiene-3,20-dione-16,17-acetonide-21acetate (29) to give 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic 16,17-acetonide acid (30);

b) reaction of 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carboxylic 16,17-acetonide acid (30) coming from step a') with dimethylthiocarbamoyl chloride in the presence of sodium iodide and triethylamine to give 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide (31);

c') reaction of 17 $\beta$ -N,N-dimethylthiocarbamoyloxycarbonyl-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide (31) coming from step b) with sodium hydrogen sulphide followed by treatment with phosphoric acid to give 17 $\beta$  carbothioic 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene 16,17-acetonide acid (32).

32. Process according to claim 30, further comprising after step d) a step e) of selective fluorination of the hydroxylic group in alpha position with respect to the sulphur atom of S-hydroxymethyl 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (33), to give S-fluoromethyl 9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ ,17 $\alpha$ -dihydroxy-3-oxoandrosta-1,4-diene-17 $\beta$ -carbothioate 16,17-acetonide (34), wherein the reaction of selective fluorination is carried out with nucleophilic fluorination reagents.

33. Process according to claim 32, wherein the said nucleophilic fluorination reagents are selected from the group consisting of bis(2-methoxyethyl) aminosulphur trifluoride, diethylamino sulphur trifluoride, and hexafluoropropyldiethylamine.

34. Process according to claim 10, further comprising a step f) of conversion of S-fluoromethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (6) into S-fluoromethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-

oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (18) (fluticasone propionate) by reaction of S-fluoromethyl 6 $\alpha$ -fluoro-9 $\beta$ ,11 $\beta$ -epoxy-16 $\alpha$ -methyl-3-oxo-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (6) with 70% hydrofluoric acid, at a temperature ranging from -30°C to room temperature, to  
5 give S-fluoromethyl 6 $\alpha$ ,9 $\alpha$ -difluoro-16 $\alpha$ -methyl-3-oxo-11 $\beta$ -hydroxy-17 $\alpha$ -propionyloxyandrosta-1,4-diene-17 $\beta$ -carbothioate (18).

35. Process according to claim 34, wherein the said reaction is carried out at a temperature ranging from -20°C to 0°C.